PATENT SPECIFICATION

NO DRAWINGS

1,082,236

1,082,236

Date of Application and filing Complete Specification: Oct. 23, 1964.
No. 43332/64.
Application made in Netherlands (No. 299783) on Oct. 25, 1963.
Complete Specification Published: Sept. 6, 1967.

Index at acceptance: —C3 R(1P1, 1P2, 1P3); **D1** P(3D, 3F2, 3G5)
Int. Cl.: —C 08 g 5/06//D 21 h

COMPLETE SPECIFICATION

Improvements in and relating to Aqueous Phenol-formaldehyde Resin Emulsions and Impregnating Fibrous Material therewith

We PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to phenol-formaldehyde resins and more particularly to aqueous emulsions of thermo-hardening low molecular weight phenolformaldehyde condensates which can be used for impregnating fibrous base materials such as for example, paper, which can then be heated and pressed to obtain resin-impregnated hard paper. The invention is particularly concerned with such emulsions and impregnated products wherein the phenol component of the resin comprises xylenol.

Sheets of paper impregnated with emulsions as referred to above may be employed to manufacture the substrata for printed wiring. To this end a number of impregnated sheets of paper, if desired together with a metal foil are united by using heat and pressure. Material to constitute supporting panels for such printed wiring must not only fulfil high electrical requirements, but it should also be susceptible of punching at room temperature or under moderate heating, to provide holes as is usual to facilitate mounting of electrical components and if desired establish electric connections between printed wirings on either side of the panel.

Punching may damage the panel in various ways to impair its electrical and mechanical properties. Most frequent is the damage in the form of cracks of the panel. Such cracks may extend not only from hole to hole, more or less at right angles to the surface of the panel, but also between the sheets of paper of the panel extending away from a hole paralllel to the surface of the panel. The latter can be recognized by a light coloured ring around the hole. In both cases moisture and water vapour may penetrate into the sheet material and have a harmful effect on its electrical properties.

When the sheet material is heated prior to punching, the damage described above occurs, during punching, to a considerably lesser extent or not at all. Depending upon the composition of the sheet material it has usually been heated between about 90° C and 140° C., prior to punching. The heating brings about an irreversible, usually small variation of the dimensions of the sheet material, which, although usually small, may nevertheless be sufficient to cause an unwanted variation in the electric properties of the printed wiring on the panel.

In the production of aqueous emulsions of thermo-hardening low-molecular weight reaction products for impregnating fibrous base materials, for example, paper or textiles, the monohydroxybenzene compound used in practice is usually phenol or cresol, or a mixture of both these. Technical mixtures of xylenols usually give rise to difficulties, since the mixture contains hydroxybenzene compounds having markedly different reactivities and functionalities with respect to formaldehyde. Technical xylenol consists mainly of a mixture of usually 5 isomers of xylenol, i.e. 1-hydroxy-2,4-dimethylbenzene, 1-hydroxy-2,5-dimethylbenzene, 1-hydroxy-2,3-dimethylbenzene, 1-hydroxy-3,4-dimethylbenzene and 1-hydroxy-3,5-dimethylbenzene; it usually contains also ethyl- and methylphenols, such as para- and meta-ethyl-phenol and para- and metacresol, and, in addition, variable small quantities of phenol. The functionality with respect to formaldehyde of these monohydroxy-

[Pric

BEST AVAILABLE COPY

benzene compounds is 1, 2 or 3. It should be observed that compounds having the same functionality may have differing degrees of reactivity with respect to formaldehyde.

The term functionality of monohydroxybenzene compounds with respect to formaldehyde denotes herein the maximum quantity of formaldehyde in mols that can be bound per mol of monohydroxybenzene compounds whilst forming methylol compounds.

When producing an impregnating resin from a mixture such as the technical xylenol described above, there is an increased risk of gel-formation, whilst the resultant emulsion may be of low stability and may impregnate non-uniformly. These difficulties are due to the discrepancies in reactivity ond functionality of the constituents of the mixture. If no special precautions are taken, a mixture of resin molecules is obtained by the condensation with formaldehyde, which have different numbers of benzene nuclei per resin molecule; the mixture includes on the one hand, low-molecular weight products and free monohydroxybenzene compounds not condensed with formaldehyde, and on the other had great quantities of high-molecular weight products.

Therefore, various measures are suggested to avoid the difficulties involved in the production of resins from xylenol mixtures and formaldehyde. It has for example been proposed to separate the mixture of xylenols by distillation into fractions each having a uniform reactivity, but this method is circuitous.

An object of the present invention is to enable a stable resin emulsion to be obtained using a technical xylenol mixture, so that products impregnated with such an emulsion can, after hardening, be punched satisfactorily at temperatures not so high as to damage the resin impregnated material, and preferably even as low as room temperature.

The present invention comprises a method of producing an aqueous emulsion of a thermohardening phenol-formaldehyde condensation product, which method comprises reacting together in water and in the presence of a basic-reacting substance, a mixture of monohydroxybenzene compounds and a molecular excess of formaldehyde or a chemical equivalent thereof, at a temperature in the range from room temperature to the boiling point of the reaction mixture, until a low-molecular weight condensation product is obtained suitable for impregnating fibrous base materials, said mixture of monohydroxybenzene compounds comprising a mixture containing not more than 60 mol % of trifunctional and not more than 25 mol % of monofunctional monohydroxybenzene compounds being at least predominantly xylenols, and an added amount of trifunctional monohydroxybenzene compound such that the whole mixture has a mean functionality of from 2.4 to 2.8 and a monoalkylphenol content not exceeding 25 mol %.

The term, chemical equivalent of formaldehyde, denotes substances capable of generating formaldehyde under the reaction conditions, particularly polymers such as paraformaldehyde.

The term, mean functionality of a monohydroxybenzene mixture, denotes herein the sum of the products of the number of mols of each monohydroxybenzene compound in a given quantity of the mixture and its functionality, divided by the sum of the number of mols of the monohydroxybenzene compounds in the said given quantity of the mixture. The mean functionality of a technical xylenol mixture usually lies below 2.4. A value lying between 2.4 and 2.8 can be obtained by adding to the technical xylenol mixture phenol or metacresol (trifunctional) or a mixture of cresols having an mean functionality exceeding 2.4.

The invention includes methods of producing resin-impregnated material or articles composed thereof, comprising impregnating fibrous base materials with such emulsions, and subsequently heat-treating to harden the resin.

The mixture of monohydroxybenzene compounds may be reacted with for example from 1.1 to 1.6 gm-mol of formaldehyde, if desired wholly or partly in the form of paraformaldehyde, per gram mol of monohydroxybenzene compound.

In the production of the impregnating resins the conventional basic catalysts may be employed, for example an alkali metal or alkaline-earth metal hydroxide or carbonate or an organic basic-reacting nitrogen compound such as a tertiary amine or quaternary ammonium compound. Examples thereof are: NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, $(C_4H_9)_3N$, and $(C_2H_5)_4NOH$. Satisfactory results are obtained by using about 0.01 gm. eq. basically reacting substance per gram mol of monohydroxybenzene compound. In some cases, however, a smaller quantity may suffice. Loosening agents and softeners such as stearamide or waxes may be added to the reaction mixture at any desired point in time. As a softener, oleamide may be used as described and claimed in our Patent Specification No 1,071,360.

After reaction under basic conditions whereby the condensation product aforesaid is produced, the reaction mixture may subsequently be acidified with an acid-reacting substance which becomes incorporated in the reaction product and forms, with the basic-reacting substance in the reaction mixture, a non-dissociated or substantially non-dissociated compound or an insoluble salt. This has a favourable effect on the electrical qualities of the resultant product and the methods described in Examples I—II below include such an acidification step.

Fibrous base materials such as paper may be impregnated in a conventional manner with the emulsions described above or in the ensuing Examples, and the products heat-treated to harden the resin, if desired under pressure, particularly for forming sheet material and especially laminates.

By way of illustration, a number of preferred methods embodying the invention for producing thermo-hardening resin emulsions and fibrous products impregnated therewith, will now be described in the ensuing Specific Examples. In the Examples, a technical xylenol mixture was employed having the following data:

content of xylenols+ethylphenols=81.2% by weight,
cresols=18.8% by weight,
content of monofunctional monohydroxybenzene compounds=16.4 mol %
bifunctional monohydroxybenzene compounds=34.4 mol %
trifunctional monohydroxybenzene compounds=49.2 mol %.
average mol. weight=119.5
average functionality=2.33

EXAMPLE I.

Production of impregnating resin.

In a reaction vessel provided with a themometer, an agitator and a reflux cooler closed by a tube containing soda lime, there were placed

12 mol of technical phenol (1258 gms which contained 128 gms of water)
18 mol of technical xylenol (2185 gms which contained 34 gms of water)
40.8 mol of formaldehyde in the form of formalin=3264 gms with 2040 gms of H_2O+CH_3OH),
0.24 mol of triethylamine=24 gms.

The mixture was heated during 30 minutes up to reflux temperature after which boiling was continued for 15 minutes under reflux. Then at a reduced pressure, 1320 mls of distillate were removed, whilst the temperature of the reaction mixture was allowed to drop to 80° C. Subsequently, 0.72 mol=204.1 gms of stearamide was added and boiling continued at 80° C, whilst stirring. The mixture was then cooled, still with stirring. When the temperature of the reaction mixture had dropped to 50° C, 80 mls of an aqueous solution containing, per 1000 mls 3 mols of $H_2N—SO_3—NH_4$ (ammonium sulphamate) were added and cooling continued, whilst stirring, to 20° C. The mixture was then ready for use as an impregnating resin.

Data: The mean functionality of all the monohydroxybenzene compound employed was 2.60.

Per mol of monohydroxybenzene compound 1.36 mol of H.CHO were used.

The impregnating resin contained at least 16% by weight of water.

EXAMPLE II.

Production of impregnating resin.

In a reaction vessel provided with a thermometer, an agitator and a reflux cooler closed by means of a tube containing soda lime, there were placed:

4 mol of technical phenol (400 gms which contained 23.5 gms of water)
8 mol of technical xylenol (971 gms which contained 15 gms of water)
18 mol of formaldehyde in the form of formalin (1481 gms, including 940.5 gms of water)
and 0.096 mol of triethylamine (9.6 gms)

The resulting mixture was heated during 30 minutes up to reflux temperature, after which boiling was continued for 13 minutes. Then 0.096 mol=18.26 gms of ammonium suphanilate was added and 630 mls distillate were removed whilst stirring and at reduced pressure, the temperature being allowed to drop to 80° C. Subsequently, 0.18 mol=51 gms of stearamide was added and heating at 80° C continued for a further 10 minutes. Then 0.048 mol=9.13 gms of ammonium sulphamate was added ($NH_4—SO_3—NH_2$), whilst the mixture was cooled, whilst stirring, to room temperature.

The resulting product was ready for use as an impregnating resin.

The mean functionality of all the monohydroxybenzene compounds employed was 2.55.

Per mol of monohydroxybenzene compound 1.5 mol of H.CHO was used.

The impregnating resin contained at least 15% of water.

EXAMPLE III.

Kraft paper (90 gms/sq. m) was impregnated in strips with the resin obtained as described in Example I, then dried in conventional manner in a hot-air tunnel, and precondensed at 140° C, after which the impregnated material was compressed to form hard paper. The product was subjected to certain experimental determinations of physical and electrical properties, of which the results are set out below, together with data as to the conditions of the compression treatment after the impregnation. The said electrical properties are the loss factor (tan δ) and dielectric constant ϵ under specified conditions.

Compression: 60 kgs/sq. cm), Pressing temperature 150° C.
Compression time 30 minutes.
Hard paper: thickness 1.8 mms;
Resin content 58%,
Water absorption after 24 hours in water at 25° C: 0.43%.
tan δ at 25° C and 120 c/sec after water absorption: 385×10^{-4}, the associated $\epsilon=5.1$.
tan δ at 25° C and 2000 c/sec after water

BEST AVAILABLE COPY

absorption 169×10^{-4}, the associated $\epsilon=4.9$.

tan δ at 25° C and 2 Mc/sec after water absorption 289×10^{-4}, the associated $\epsilon=4.5$.

Resistivity at 25° C and 300 V after water absorption 9×10^{12} ohm. cm.

The hard paper obtained by means of the impregnating resins embodying the invention appeared to allow punching excellently at a temperature below 90° C, avoiding the difficulties described earlier. It was found that the emulsions could be stored for a considerable time without the imuregnating power being reduced.

Articles composed of resin-impregnated fibrous base material may be manufactured by applying the process described above in a manner analogous to conventional known procedures, that is to say, by shaping the resin-impregnated material before hardening, and by working of the hardened product, to obtain a desired article.

WHAT WE CLAIM IS:—

1. A method of producing an aqueous emulsion of a thermo-hardening phenol-formaldehyde condensation product, which method comprises reacting together in water and in the presence of a basic-reacting substance, a mixture of monohydroxybenzene compounds and a molecular excess of formaldehyde or a chemical equivalent thereof as herein defined, at a temperature in the range from room temperature to the boiling point of the reaction mixture, until a low-molecular weight condensation product is obtained suitable for impregnating fibrous base materials, said mixture of monohydroxybenzene compounds comprising a mixture containing not more than 60 mol % of trifunctional and not more than 25 mol % of monofunctional monohydroxybenzene compounds being at least predominantly xylenols, and an added amount of trifunctional monohydroxybenzene compound such that the whole mixture has a mean functionality of from 2.4 to 2.8 and a monoalkylphenol content not exceeding 25 mol %.

2. A method as claimed in Claim 1, wherein the said mixture of monohydroxybenzene compounds consists of a technical xylenol mixture, the mean functionality of which is adjusted to a value of from 2.4 to 2.8 by addition of phenol, metacresol or a mixture of cresols.

3. A method as claimed in Claim 1 or Claim 2 wherein after the reaction under basic conditions giving the condensation product aforesaid, the reaction mixture is acidified by adding an acid-reacting substance which becomes incorporated in the reaction product and forms, with the basic-reacting substance in the reaction mixture, a non-dissociated or substantially non-dissociated compound or an insoluble salt.

4. A method of producing an aqueous emulsion of a thermo-hardening phenol-formaldehyde condensation product substantially as herein described with reference to either of the foregoing specific Examples I and II.

5. An aqueous emulsion of a thermo-hardening phenol-formaldehyde condensation product produced according to the method claimed in any one preceding Claim.

6. A method of manufacturing resin-impregnated fibrous base material or articles composed of such material, which method comprises impregnating fibrous base material with an emulsion as claimed in Claim 5, and subjecting to a heat treatment to harden the resin.

7. A method of manufacturing resin-impregnated fibrous base material or articles composed thereof substantially as herein described with reference to the foregoing specific Example III.

8. Resin-impregnated fibrous base material or articles composed thereof, when manufactured by the method claimed in Claim 6 or Claim 7.

T. D. THREADGOLD,
Chartered Patent Agent,
Century House,
Shaftesbury Avenue,
London, W.C.2,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1967.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.